

Borane-containing polyolefins: synthesis and applications

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Abstract

This article summarizes the experimental results in the synthesis and applications of borane containing polyolefins. It is becoming clear that the introduction of borane groups into polyolefins, such as polyethylene (PE) and polypropylene (PP), is a valuable route for achieving their functionalization, which has been a long scientific challenge and industrial needed technology. The trialkylborane moieties, unlike other organic functional groups, are stable to early transition metal (Lewis acid) complexes and compatible with olefin monomers. Therefore, borane-containing monomers can be effectively incorporated into polyolefins via Ziegler–Natta and metallocene copolymerization reactions. In turn, the borane group that is incorporated into the polymer not only can be quantitatively converted to a hydroxy group, but it also can be transformed into a stable polymeric radical that then initiates a living free radical polymerization of the functional monomers. The functional group and functional group concentration are basically governed by the monomers that are introduced. The resulting graft and block copolymers, having well-controlled molecular structures, would be very difficult to prepare by existing methods. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ziegler–Natta catalyst; Metallocenes; Graft copolymer; Block copolymer

1. Introduction

In organic synthesis, borane is known as one of the most versatile reagents [1] in the functionalization of organic molecules. However, the use of the borane group in polymers is very rare. In the early publications, only few cases of using borane reagents in the modification of unsaturated polymers have been reported, specifically in the hydroboration of polydienes [2]. The method was limited by the availability of unsaturated polymers.

The initial thought in our study of borane containing polymers stemmed from the need to develop a new functionalization chemistry for polyolefins, including polyethylene (PE) and polypropylene (PP), which represent more than 50% of commercial polymers [3] produced. Unfortunately, this class of polymers suffers from the lack of functional (polar) groups, which has limited many of their commercial applications [4–6],

particularly those in which adhesion, dyeability, printability or compatibility with other materials is paramount.

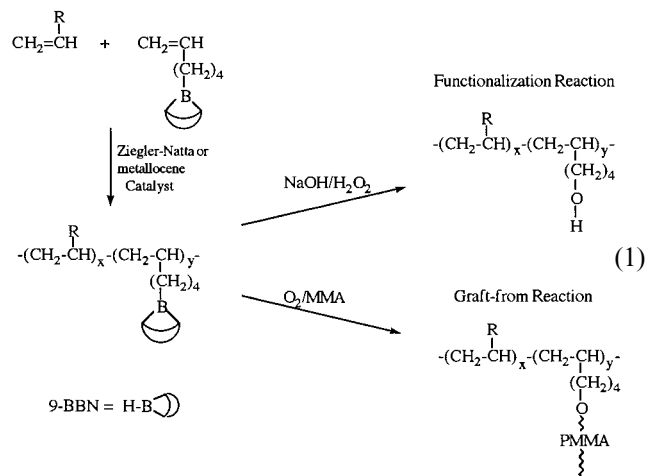
It is well known that the transition metal coordination polymerization [7] (using Ziegler–Natta and metallocene catalysts) is the most important method for preparing polyolefins, but the direct polymerization of functional monomers using this method is very difficult because functional groups (e.g. –OH, –NH₂, –COOH) preferentially coordinate with the active sites (early transition metal complexes) [8,9] and poison the catalyst. Thus, polymerization is inhibited. A great deal of the research in this problem has focussed on the chemical modification of pre-formed polymers. Unfortunately, polyolefins (PE and PP) are extremely resistant to chemical modification due to their inert chemical nature and crystallinity. In many cases, the free radical reaction process involves severe side reactions, such as cross-linking and degradation [10] of the polymer chain, that are very undesirable. It is clear that there is a fundamental need to develop a new chemistry that can address this challenge of preparing functional polyolefins.

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2. Borane monomer approach

In the past few years, we have discovered a very interesting functionalization chemistry that involves the use of borane-containing olefins [11–15] as the comonomers in Ziegler–Natta (Z–N) and metallocene polymerization reactions. Eq. (1) illustrates the general reaction scheme.



The borane-containing monomer can effectively copolymerize with all the α -olefins by choosing the appropriate catalyst system. The incorporated borane groups in the polyolefin serve as the reactive sites for selective functionalization under mild reaction conditions. It is highly desirable to convert the borane group to a polymeric free radical species that can initiate free radical graft-from polymerization of the functional monomers, such as acrylics and methacrylics. Such a reaction dramatically increases the efficiency of the borane group. Hundreds and thousands of functional groups can then be incorporated into the polyolefin polymer chain by a single borane group. The functional groups introduced are pre-determined by the monomer that is used. In addition, the resulting graft and block copolymers, containing both polyolefin and functional polymer segments, are very desirable functional polymers. These polymers not only provide high concentration of functional groups, but also preserve many of the unique polyolefin properties, such as crystallinity, melting point and hydrophobicity. In addition, block and graft copolymers are known to be the best compatibilizers for improving interfacial interactions in polymer blends and composites.

The initial idea of using borane monomers, ω -alkenylboranes [16–18], for polyolefin functionalization was based on three considerations: (a) The stability of borane to transition metal catalysts. Because trialkylborane is a Lewis acid it has a very good chance of coexisting with the catalyst. In addition, the boron atom is relatively small and steric protection can be

effectively applied if needed. (b) The solubility of borane monomers and polymers in the hydrocarbon solvents (hexane and toluene) used in Ziegler–Natta polymerization. A soluble growing polymer chain is essential to obtain a high molecular weight polymer. (c) The versatility of borane groups. The borane groups incorporated into the polyolefins were not only inter-converted to various functional groups (such as hydroxy) but also transformed to polymeric radicals for graft-from reactions to prepare polyolefin graft copolymers.

3. Copolymerization reactions of borane monomers and α -olefins

As shown in Eq. (1), the borane monomer, 5-hexenyl-9-BBN (9-BBN: 9-borabicyclo[3.3.1]nonane), is copolymerized with an α -olefin by using commercial Ziegler–Natta heterogeneous catalysts, such as $\text{TiCl}_3 \cdot \text{AA}$ (AA: aluminum reduced and activated)/ Et_2AlCl , or homogeneous metallocene catalysts [19,20], such as Cp_2ZrCl_2 (Cp: cyclopentadiene), $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (Ind: indene), and $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{N}^t\text{Bu})]\text{TiCl}_2$, with methylaluminoxane (MAO). This chemistry is very general and can be applied to various α -olefins, such as ethylene, propylene, 1-butene, 1-octene and their mixtures, with the appropriate choice of catalyst. In general, the homogeneous metallocene catalysts were very effective for copolymerizations involving ethylene, and isospecific Ziegler–Natta heterogeneous catalysts were used for copolymerizations without ethylene.

Table 1 summarizes the experimental results [21] of the copolymerization reaction between 5-hexenyl-9-BBN and ethylene. Overall, the homogeneous zirconocene/MAO catalysts, especially $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ which has strained ligand geometry [19] (due to an ethylene bridge between two indene ligands) and an open active site, accommodate the relatively large size of the borane monomer. About 50–60% of the borane monomers were incorporated into the PE copolymers after about half hour reaction time. Comparing runs I-1 to I-4, the concentration of borane groups in the polyethylene is basically proportional to the concentration of borane monomer feed. It is very unexpected that the catalyst activity systematically increases with the concentration of borane monomer in the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system. Obviously no retardation due to the borane groups is shown in these cases. The copolymerization of borane monomers in the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system (shown in run I-6) is significantly more difficult. Only 1.22 mol% of borane monomer was incorporated into the PE copolymer, even when high concentration of borane monomer was used. On the other hand, the heterogeneous $\text{TiCl}_3 \cdot \text{AA}/\text{Et}_2\text{AlCl}$ catalyst shows no detectable amount

Table 1

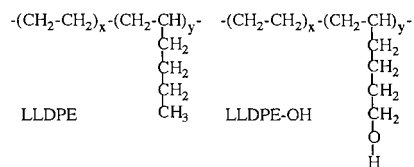
A summary of copolymerization reactions [16,17] between ethylene (m_1) and 5-hexenyl-9-BBN (m_2)

Run number	Catalyst type ^a	Comonomers m_1/m_2 (psi ^b g ⁻¹)	Reaction temperature/time (°C min ⁻¹)	Catalyst activity (kg mol ⁻¹ h ⁻¹)	Borane in copolymer (mol%)
I-1	I	40/0	30/70	350	0
I-2	I	45/0.22	30/30	480	1.25
I-3	I	45/0.61	30/30	660	2.15
I-4	I	45/0.82	30/30	850	2.30
I-5	II	45/0	30/70	110	0
I-6	II	45/5	30/70	210	1.22
I-7	III	80/10	60/110	1.3	0

^a Catalysts: Et(Ind)₂ZrCl₂/MAO (I), Cp₂ZrCl₂/MAO (II) and TiCl₃·AA/Et₂AlCl (III). Solvent: 100 ml toluene.^b Corresponding to 0.38 mol l⁻¹.

of the borane group in the copolymer as shown in run I-7.

The borane groups in the polymers were converted to the corresponding hydroxy groups by reacting with NaOH/H₂O₂ reagents at 40°C for 3 h. The effective interconversion in the heterogeneous reaction condition is due to the high surface area of borane groups in the semi-crystalline microstructure of the copolymers. The borane groups located in the flexible side chains may migrate to the surfaces or amorphous phases where the chemical reagents can be easily reached. It is very interesting to note that the resulting functionalized polyethylene (LLDPE-OH), containing a hydroxy group located at the end of side chain, is structurally similar to that of linear low density polyethylene (LLDPE) as shown below:



It is very interesting to extend the functionalization chemistry to other polyolefins, especially the use of commercially-available heterogeneous Ziegler–Natta catalysts, such as the isospecific TiCl₃·AA/Et₂AlCl catalyst. In general, the borane monomer behaves like a high α -olefin in the Ziegler–Natta catalyst, the bigger the size of the monomer the lower the reactivity. Fig. 1 shows the plot of 5-hexenyl-9-BBN (mol%) in the copolymers versus reaction time during three copolymerization reactions [22,23] of 1-propene/5-hexenyl-9-BBN, 1-butene/5-hexenyl-9-BBN, and 1-octene/5-hexenyl-9-BBN, with 1:1 comonomer mole ratio, by using TiCl₃·AA/Et₂AlCl catalyst.

The copolymer compositions of poly(1-octene-co-5-hexenyl-9-BBN) are quite flat and are close to the ideal 50 mol% mark as shown in Fig. 1(a). Only a small increase in borane content in the copolymer with the increasing conversion suggests a slightly higher reactivity of 1-octene as compared to 5-hexenyl-9-BBN. In the

1-butene case, the fluctuation of the copolymer composition is much more dramatic, especially at the beginning of the copolymerization. The reactivity of 1-butene is significantly higher than that of 5-hexenyl-9-BBN. In fact, if we extrapolate the composition to time = 0 in Fig. 1(b), the copolymer produced at the very beginning of the reaction contains ca. 7 mol% 5-hexenyl-9-BBN. The initial incorporation of the borane monomer in the polypropylene copolymer was very small, as shown in Fig. 1(c). Only 1.6 mol% was incorporated in the first 0.1 h, which increased to 3.5 and 6 mol% after 1 and 2 h, respectively. The reactivity of the monomers is obviously different: propylene \gg 1-butene $>$ 1-octene \sim 5-hexenyl-9-BBN. Basically, the reactivity of 5-hexenyl-9-BBN follows the same trend in heterogeneous Ziegler–Natta polymerization: smaller size equals higher reactivity. The reactivity becomes less variable in high α -olefins.

In the batch reaction with the fixed monomer ratio of propylene/5-hexenyl-9-BBN, the copolymer obtained is either a narrow compositional distribution at low conversion (at extremely low yield) or a broad composition

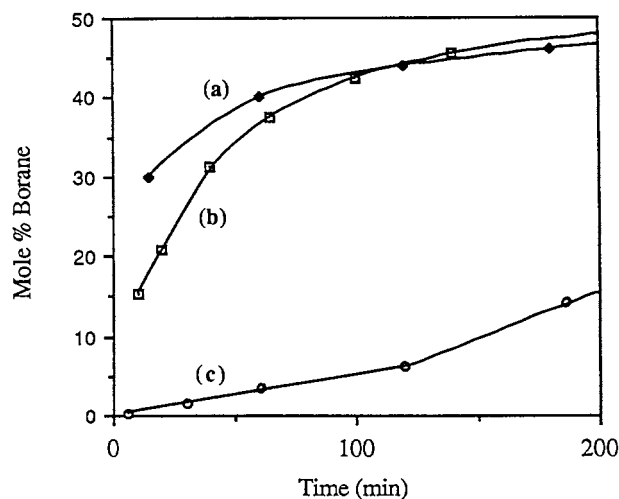


Fig. 1. Plots of 5-hexenyl-9-BBN (mol%) in (a) poly(1-octene), (b) poly(1-butene) and (c) polypropylene copolymers vs. reaction time.

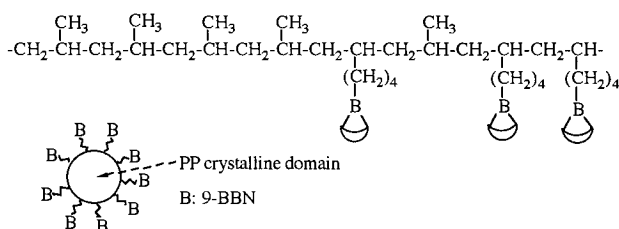
Table 2

The summary of copolymerization of 1-propene (m_1) and 5-hexenyl-9-BBN (m_2) by continuous reaction and $\text{TiCl}_3 \cdot \text{AA}/\text{Et}_2\text{AlCl}$ catalyst

Run number	Comonomers m_1/m_2	Reaction temperature/time ($^\circ\text{C}$ h $^{-1}$)	Yield (%)	Borane in copolymer (mol%)	Intrinsic viscosity (h)	M_v
II-1	100/0	25/2	93	0	2.07	230 000
II-2	95/5	25/3	87	1.7	1.95	210 000
II-3	90/10	25/4	72	3	1.78	183 000
II-4	85/15	25/5	55	6	1.71	174 000

distribution at high conversion. It is feasible to engineer the incorporation of the borane group sequence in the PP copolymer by controlling the monomer feed ratio during the copolymerization. Usually the more reactive 1-propene monomer was added periodically in decreasing amounts to account for the consumption of the borane monomer during the reaction. Table 2 summarized the experimental results [23] of a copolymerization between 1-propene and 5-hexenyl-9-BBN. The 1-propene monomer was added six times at 30 min intervals with the consecutive reduced amounts.

In general, the copolymerization reactions via a continuous addition of 1-propene were very effective in producing functionalized PP copolymers with high molecular weight, at high yields and with a controllable concentration of functional groups. In addition, this process can produce PP copolymers with 'brush-like' structures [24,25] as shown below.

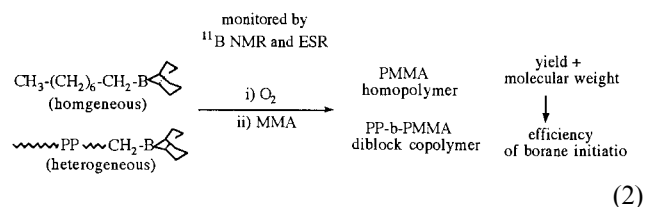


Owing to the fluctuation of 1-propene concentrations during the copolymerization process, the side chains (with functional groups) in the polymer are concentrated at the chain end of the polyolefin backbone. The functionalized PP with the 'brush-like' structure has many interesting physical properties. The consecutive long sequence of propylene units in the polymer chain can be effectively crystallized to form an insoluble support structure, and the flexible side chains containing borane groups are excluded from the crystalline domain to the surface. This type of polymer structure not only possesses a desirable concentration of functional groups, but also preserves the original physical properties, such as crystallinity, melting point and thermal stability, of pure polypropylene. The polypropylene sequence in the copolymer can co-crystallize with pure polypropylene. The functional group located at the end of each side chain preferentially moves away from the hydrophobic PP crystalline matrix to the surfaces, which can then interact with other materials.

4. Selective autoxidation reaction of alkyl-9-BBN

As discussed above, it is very desirable to transform the borane group into the polymeric radical that can polymerize functional monomers, such as acrylics and methacrylics. Such a graft-from reaction [14,15] could incorporate hundreds and thousands of functional groups into a polyolefin chain via a single borane group. Although the free radical polymerization by the oxidation adducts [26–28] of trialkylboranes, such as triethylborane and tributylborane, were reported in the late 1950s, the experimental results showed only a very low percentage of borane groups participating in the polymerization reactions. The general sense of the borane oxidation reaction [29–31] was very complicated with many intermediates produced during the oxidation process. There were no experimental results in the selective autoxidation of asymmetrical borane moieties, such as alkyl-9-BBN, which is essential in the transformation of borane group to a polymeric radical in the preparation of polyolefin graft and block copolymers.

A systematic study was carried out to investigate the autoxidation reactions of ethyl-9-BBN and its corresponding 9-BBN containing polypropylene (PP-9-BBN), which has a borane group located at the PP chain end (preparation will be discussed later). The oxidation reactions were monitored by ^{13}C -, ^{11}B -NMR and ESR techniques as illustrated in Eq. (2).



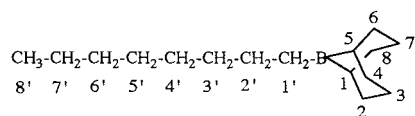
The oxidation adducts were used in the subsequent free radical polymerization reactions of methyl methacrylate (MMA), and will be discussed in the next section.

The borane moieties, having one linear primary alkyl and two cyclic secondary alkyl groups, are readily oxidized by oxygen at ambient temperature. Fig. 2 shows the ^{11}B -NMR spectrum [32] of the oxidation adducts for octyl-9-BBN/ O_2 with and without the MMA monomers presence.

The oxidation adducts of octyl-9-BBN/O₂ are very complicated, and include various BOR₂, BO₂R and BO₃ species and unreacted octyl-9-BBN. However, in the presence of MMA, the oxidation reaction is much more well defined with the predominant mono-oxidation adduct BOR₂ and nearly complete oxidation of octyl-9-BBN. The experimental results indicate that the MMA monomers are quite effective in reacting with the mono-oxidized adduct and preventing any further oxidation reactions that could be associated with the intermolecular reactions between the oxidized adducts. As will be discussed later, the mono-oxidized adduct of octyl-9-BBN initiates the polymerization of MMA.

The oxidation mechanism in these reactions is very interesting, especially the oxidation selectivity between one linear B–C primary alkyl and two cyclic B–C secondary alkyls with double chair-form structure. Fig. 3 compares the ¹³C-NMR (DEPT-135) spectra [33] of octyl-9-BBN and its oxidation adducts.

In Fig. 3(a), the chemical shifts at 33.2 and 23.4 ppm are assigned to C-2,4,6,8 and C-3,7 in the bicyclononane structure as shown below:



It is difficult to see the chemical shifts corresponding to the bridge heads (C-1 and C-5) and C-1' owing to the

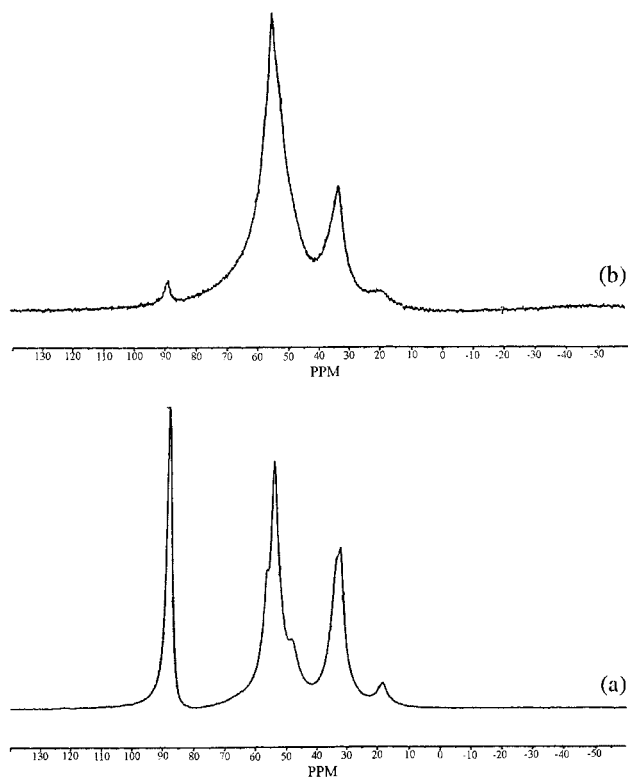


Fig. 2. ¹¹B-NMR spectrum [32] of the oxidation adducts for octyl-9-BBN/O₂ (a) with and (b) without the MMA monomers presence.

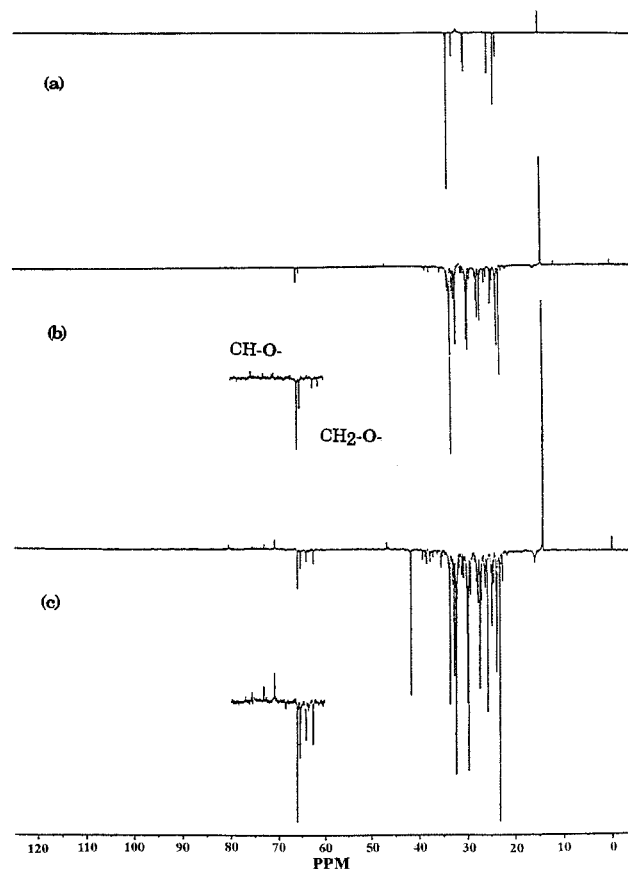
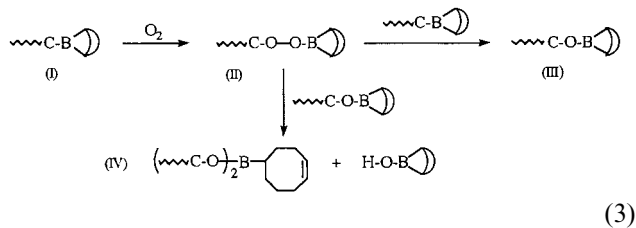


Fig. 3. The ¹³C-NMR (DEPT-135) spectra of (a) octyl-9-BBN and its oxidation adducts with various mole ratio of oxygen, (b) 50% and (c) 100%.

rapid relaxation associated with the *J'* coupling with boron. The peaks at 14.3 and 22.9 ppm are assigned to C-8' and C-2', respectively, in the linear alkyl group. The autoxidation reaction took place in octyl-9-BBN after exposing it to 50 mol% (versus borane) of oxygen at ambient temperature. Fig. 3(b) shows a new major peak at 65.9 ppm, accompanied by several minor peaks between 66 and 60 ppm. The negative intensities indicate the presence of several methylenes with adjacent oxygen due to oxidation occurring between the boron and the adjacent CH₂ of the octyl group. The selectivity diminished somewhat with increased oxygen addition. As shown in Fig. 3(c), several additional new weak peaks with positive intensity appear between 70 and 75 ppm, which correspond to the oxidation occurring between the methine and the boron in the borabicyclononane group. The overall experimental results clearly show that the oxygen insertion into alkyl-9-BBN prefers the B–C linear alkyl group to the B–C bicyclic ring. The stable double chair-form structure may prevent the unfavorable ring strain increase due to the insertion of a peroxy group into the chair-form structure [33,34]. The double and triple oxidized adducts, i.e. BO₂R and BO₃ species, may be a result of the inter-

molecular reaction of the mono-oxidized adduct (II) as illustrated in Eq. (3).

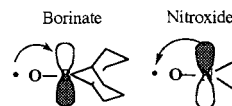


It is very logical to predict the facile intermolecular reaction between peroxy borane (II) and unreacted alkylborane (I) to produce alkoxyborane (III), and between peroxy borane (II) and alkoxy borane (III) to produce the di-oxidized adduct (IV). The last reaction breaks the stable borabicyclononane ring, which then allows the third oxidation reaction to take place between the B–C methine bond. On the other hand, in the presence of MMA monomers (usually the concentration ratio of [MMA]/[borane] > 100) the peroxyborane (II) that is formed reacts with MMA at rt and initiates the free radical polymerization. Therefore, the intermolecular reactions between the borane species are subdued.

ESR measurement [32] provides direct evidence of the radical species. As shown in Fig. 4, a singlet ESR

signal was observed in the O₂ oxidized PP-9-BBN sample, which has the *g*-value of 2.0155, corresponding to peroxy (ROO*) or alkoxy (RO*) radicals.

The radical appears to be very stable for many days, which may be due to its immobilization in the solid PP support. Upon addition of the MMA monomers, the ESR signal changes to a hyperfine splitting pattern, indicative of a propagating PMMA carbon radical (R*). Because the peroxy radical (ROO*) is incapable of initiating the free radical polymerization, the stable radical formed in the O₂ oxidation of PP-9-BBN must be the alkoxy radical (RO*). It is very interesting to note that the homolytical cleavage of peroxyborane may be enhanced by the formation of a stable borinate radical (B-O*) as illustrated below:



Compared with the known stable nitroxide radicals, such as the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical [35], in which the radical is stabilized by electron-donating of the lone-pair electrons in p-orbital of nitrogen to the free radical, the radical in the borinate group may demonstrate a reverse stabilization mechanism by back-donating electron density to the empty p-orbital of boron.

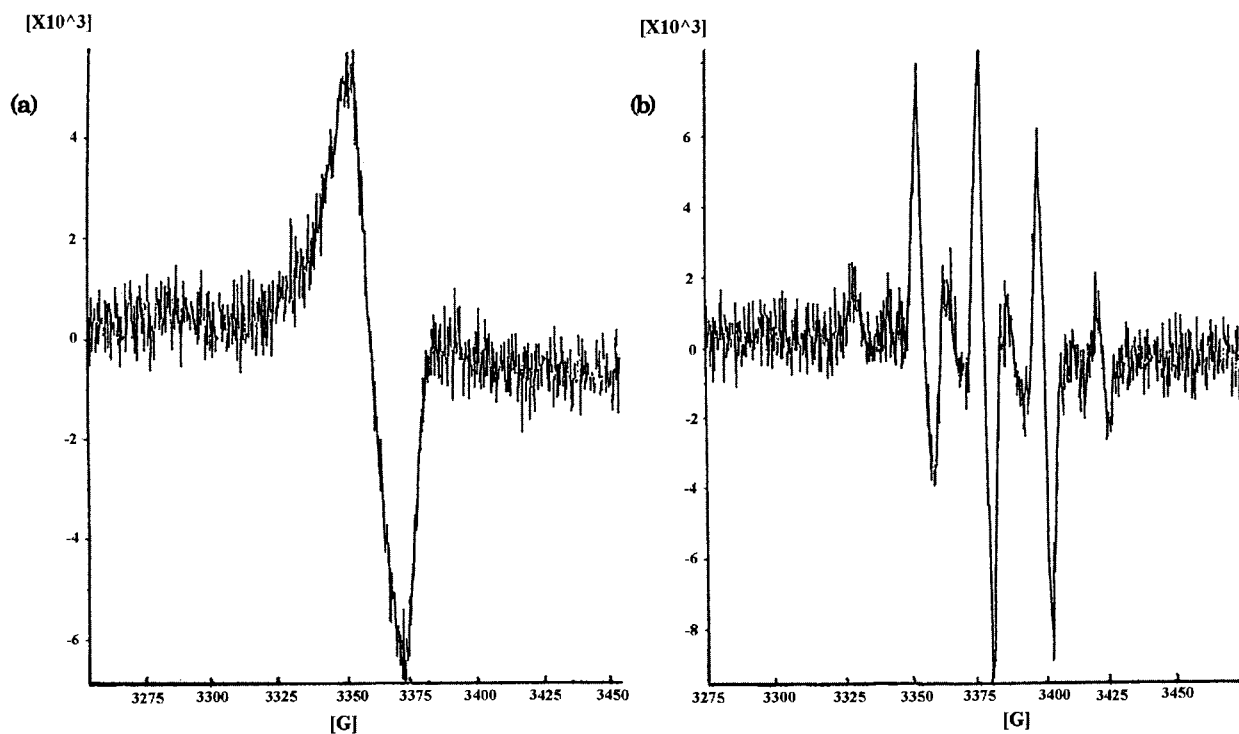


Fig. 4. ESR spectrum of (a) the O₂ oxidized PP-9-BBN sample, (b) upon addition of the MMA monomers.

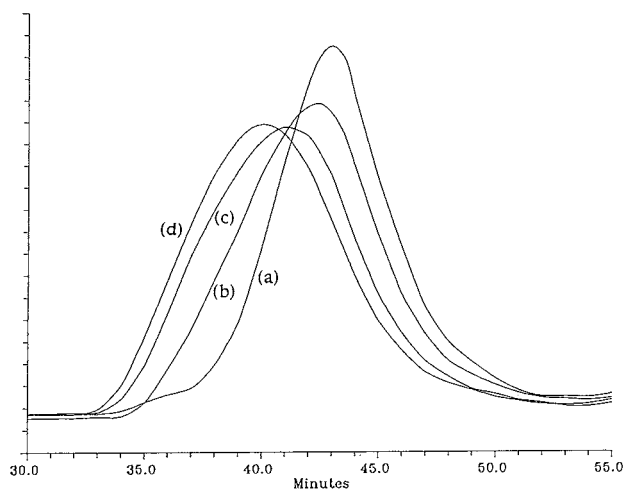
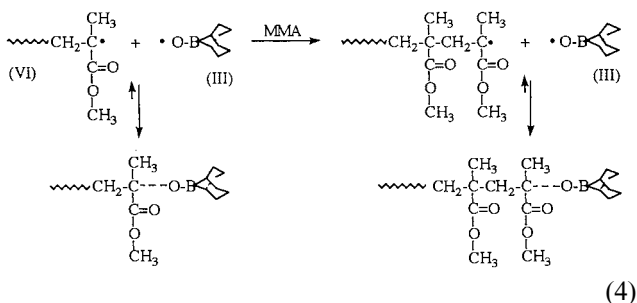


Fig. 5. The comparison of GPC curves between PEMA homopolymers with various reaction times (a) 1 h, (b) 3 h, (c) 5 h and (d) 24 h.

5. Free radical polymerization by oxidative adducts of alkyl-9-BBN

As discussed, peroxyborane (II) behaves very differently from regular peroxides and decomposes by itself even at ambient temperature to generate an alkoxy radical (C–O*) and a borinate radical (B–O*). In the presence of free radical-polymerizable monomers, such as methacrylates, vinyl acetate, acrylonitrile etc, the alkoxy radical initiates a radical polymerization [36] at ambient temperature. However, the borinate radical is too stable to react with the monomer, but it may form a weak and reversible bond with the growing chain end during the polymerization reaction as illustrated in Eq. (4).



Upon the dissociation of the electron pair, the growing chain end (VI) can then react with the monomer, for example methyl methacrylate (MMA), to extend the polymer chain. The resulting new chain-end radical immediately forms a weak bond with the borinate radical (III). This process minimizes the undesirable chain transfer reaction and termination (coupling and disproportionation) reaction between the two growing chain ends.

In a typical example, 1-octyl-9-BBN (0.042 g) was mixed with an ethyl methacrylate (7 g) monomer and

25 ml of THF or benzene solvent in a septum-capped 250 ml flask equipped with a high vacuum stopcock. The reaction was initiated by injecting O₂ into the reaction flask at rt. To assure the formation of a 'stable' initiator, only 50% of the oxygen (versus borane) was added and the unreacted oxygen was vacuum-removed within 1 h. Under this reaction condition, only a few percent of the borane was oxidized. The slow reaction was mainly due to the inhomogeneous mixing between the two very dilute reagents: borane reagent in solution and oxygen gas. However, the resulting initiators were sufficient to initiate the polymerization and poly(ethyl methacrylate) (PEMA) was periodically removed. Fig. 5 shows the GPC curves of PEMA polymers with various reaction times. The first sample was removed after 1 h of reaction under the coexistence of alkyl-9-BBN and O₂. In other words, the propagating chain ends increased with the polymerization time. After removal of the oxygen, the propagating chain ends became constant and the consecutive samples were produced under a constant number of active sites. This clearly shows that the polymer continuously increased its molecular weight during the entire polymerization process. The molecular weight distribution stays very constant, with the polydispersity index (PDI = M_w/M_n) of about 2.5. The relatively broad molecular weight distribution, compared with those in living anionic polymerization cases, may be attributed to the slow initiation in the first hour (as discussed above). In other words, the initiation of each polymer chain took place at a different time. Fig. 6 compares the yields and molecular weights of poly(methyl methacrylate) (PMMA), PEMA and Poly(*t*-butyl methacrylate) (Pt-BMA) during similar radical polymerization conditions. The molecular weight was determined by GPC measurement using polystyrene as the calibration standard.

The linear increase of molecular weight versus polymer yield indicates a constant polymer chain number after the oxidation reaction. This also implies a 'stable' propagating chain end without significant termination and chain transfer reactions. In fact, high molecular weight (more than 1 million) polymers of PMMA and PEMA with relatively narrow PDIs (< 3) have also been prepared. Such polymer structures would be very difficult to achieve by traditional free radical polymerization.

The simplicity of this 'stable' radical polymerization process, which occurs at ambient temperature with the injection of oxygen (or air) to alkyl-9-BBN, is remarkable. The lack of chain-transfer and termination, both disproportionation and coupling reactions, must be associated with the existence of 'dormant' species that are produced in situ during the formation of the initiator.

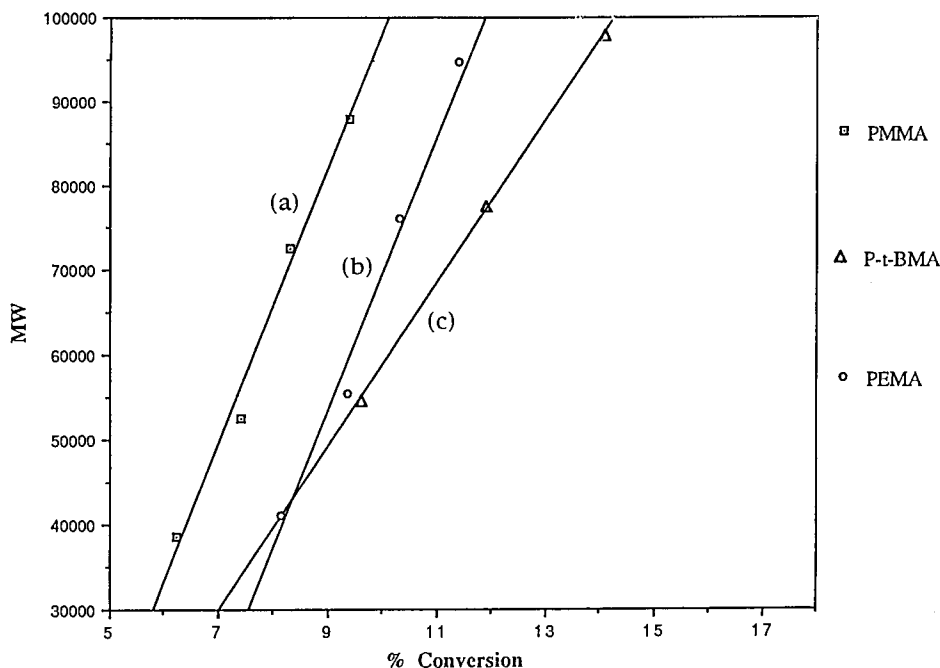
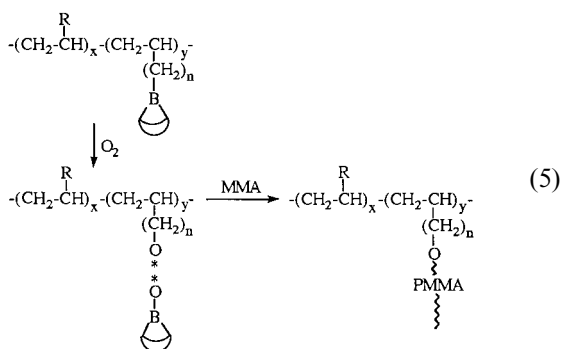


Fig. 6. Plots of molecular weight and yield of (a) PMMA, (b) PEMA and (c) Pt-BMA polymers.

6. Synthesis of polyolefin graft copolymers via borane/ O_2 adducts

This radical polymerization chemistry using a borane/ O_2 adduct as the initiator has been directly applied to the borane-containing polyolefin cases. In other words, the borane-containing polyolefin is transformed into the polymeric free radicals (via the O_2 oxidation reaction of the borane groups). The former polymeric radicals can then initiate a living free radical polymerization of methacrylates, acrylamide, vinyl acetate, acrylonitrile, etc. at room temperature as illustrated in Eq. (5).



In this case, the free radical polymerized polymers are chemically bonded to the side chains of the polyolefin. Some interesting polymers [14,15], such as PE-g-PVA, PE-g-PAN, PP-g-PMMA, PP-g-PVA, PP-g-PAN, EP-g-PMMA and butyl-g-PMMA, have been synthesized with controlled compositions and molecular microstructures. Most of them would be otherwise very difficult to prepare using existing methods.

Table 3 summarizes the experimental results of PP-g-PMMA copolymers [37]. The comparison among runs 1–4 shows the sensitivity of the oxygen addition to the graft efficiency. Even though the final stoichiometry of oxygen to boron should be 1:1, the best results in this heterogeneous reaction system are realized when the O_2 is introduced slowly so that $O \ll B$ at any given time. The polarity of the solution can also effect the graft reaction. THF is a very good solvent in this reaction. A nonpolar solvent, such as benzene, slows down the graft-from reaction, which may be due to the solubility of O_2 in the solvent. In run 5 the oxygen was introduced by diffusion of air through a rubber septum that was tightly installed on the top of the reactor. The insufficient O_2 in this process leads to a low percentage of PMMA formation.

Similar graft-from reactions have been extended to various polyolefin backbones. Satisfactory results were obtained for both homogeneous (PE, PP and PB cases) and heterogeneous (PO, EP and Butyl rubber cases) reaction conditions. In one homogeneous case, the commercial EPDM rubbers, including poly(ethylene-co-propylene-co-1,4-hexadiene) and poly(ethylene-co-propylene-co-5-ethylidene-2-norbornene), were used to prepare EP graft copolymers [38]. Table 4 summarizes some of the experimental results. The hydroborated EPDM rubbers were usually mixed with methyl methacrylate in a THF solution. Upon exposure to oxygen, the graft-from reaction took place at rt. The total oxygen used was only 50% (versus borane groups) to ensure the occurrence of the selective oxidation reaction as discussed before. The graft-from reaction was terminated by precipitating polymer in MeOH.

Chain end unsaturated polypropylene was prepared using a homogeneous $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst. Both internal and external double bonds were observed, which are due to the β -proton elimination from 1,2- and 2,1-inserted propagating chain ends, respectively. The higher the reaction temperature the higher the olefin concentration, and the lower molecular weight. This temperature–molecular weight relationship was confirmed by $^1\text{H-NMR}$ and GPC results. It is very interesting to note that the ratio of external and internal olefins is very dependent on the reaction temperature. At elevated temperature (such as 80°C), the external double bond is the major product.

The chain end unsaturated polypropylene was used as the starting material for the preparation of diblock copolymers. The hydroboration reactions were carried out under heterogeneous reaction conditions by suspending a powder form of polypropylene in THF. Slightly excess 9-BBN was used to ensure complete reaction. The reaction mixture was stirred at 55°C for 5 h before removing the polymer powder from solution by filtration. To examine the efficiency of the reaction, some of hydroborated polymer was oxidized to obtain an hydroxylated polymer by using $\text{NaOH}/\text{H}_2\text{O}_2$ reagents at 40°C for 6 h. The olefinic chemical shifts between 4.7 and 5.6 ppm disappear to the limit of NMR sensitivity. Apparently, both hydroboration and oxidation reactions were not inhibited by the insolubility of polypropylene. On the other hand, most of the

9-BBN terminated polypropylene (PP-9-BBN) was subjected to the oxidation reaction by oxygen in the presence of free radical polymerizable monomers, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA) and styrene. The in situ formation of a polymeric radical at the polymer chain end initiated radical polymerization. The radical polymerization was terminated by precipitating the polymer mixture in MeOH. The product, isolated by filtration and washed with MeOH, was then subjected to fractionalization. In the PP-b-PMMA case, the sample was extracted with refluxing acetone and heptane, respectively, in a Soxhlet apparatus for 24 h. The heptane-soluble fraction is basically pure PP, and the acetone-soluble fraction contains only PMMA. The major fraction ($> 60\%$), insoluble in heptane and acetone but soluble in toluene at elevated temperatures, is PP-b-PMMA diblock copolymer. Fig. 7 compares the GPC curves between the starting PP homopolymer and the resulting PP-b-PMMA diblock copolymer.

The molecular weight more than doubled from $M_n = 13\,000$ to $M_n = 29\,000 \text{ g mol}^{-1}$, and molecular weight distribution (MWD) only increased slightly from 1.48 to 1.69. The narrow molecular weight distribution indicates a living polymerization reaction. The resting state of a growing chain end must form a weak bond with the borinate radical, which minimizes the undesirable chain transfer and termination reactions, namely, radical coupling and disproportionation reactions between two

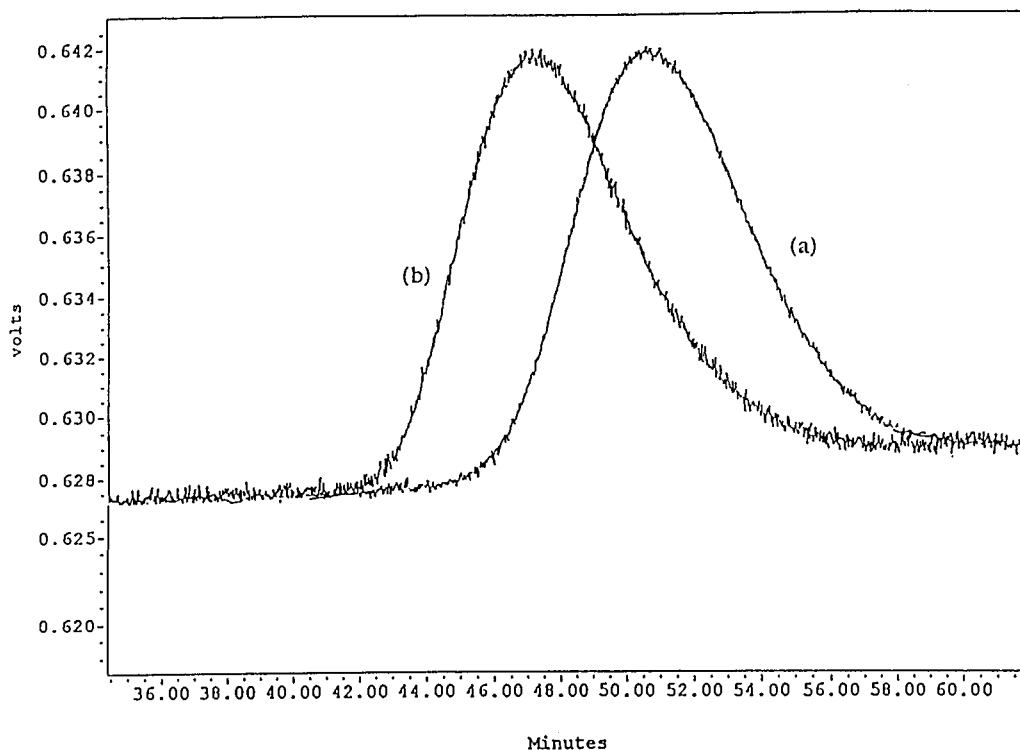


Fig. 7. GPC curves of (a) PP and (b) the corresponding PP-b-PMMA copolymer.

Table 5
A summary of PP-b-PMMA diblock copolymers

PP (g)	Reaction conditions			Fractionalization product			Mol% MMA in diblock copolymer
	MMA (g)	Solvent (ml)	Oxygen (ml)	Acetone (g)	Heptane (g)	Insoluble (g)	
0.5	5	THF/5	0.44	0.25	0.18	0.72	33
0.5	5	Benzene/5	0.44	0.16	0.08	0.90	28
13.3	80	THF/80	10.8	^a	^a	23.5	45

^a Undetermined.

growing chain ends. These results are consistent with the control reactions using alkyl-9-BBN as the radical initiator, which showed 'stable' radical polymerization of MMA under similar reaction conditions.

The detailed experimental conditions and results are summarized in Table 5. All reactions were started from the same PP sample with $M_n = 13\,000$ and $M_w/M_n = 1.48$. The reactions took place at ambient temperature for 16 h. The overall yield of diblock copolymer is between 60 and 80%, which is very encouraging considering that there was only one borane initiator in each polymer chain, and some (up to 20%) of the polymer chains did not have a borane group. All three reactions, including hydroboration, oxidation and radical polymerization, must be very effective despite the heterogeneous conditions. The mol% of MMA in each copolymer can be controlled by monomer concentration and reaction time. Slightly better results, with less homopolymer, using benzene solvent may be due to the slow diffusion of oxygen in the reaction media, which offers better selectivity in the oxidation of PP-9-BBN.

The same radical chain extension was also applied to other free radical polymerizable monomers, including ethyl methacrylate (EMA), vinyl acrylate (VAc), butyl acrylate (BA) and styrene. It is very interesting to note that a significantly lower incorporation of styrene monomers was observed, which may be associated with the acidic nature of the borane initiator. The acid–base interactions between borane and monomers containing basic oxygen, such as MMA, EMA, VAc and BA, may produce a 'cage' effect, with monomers surrounding the catalyst leading to effective initiation and polymerization. Styrene monomers, lacking such a specific interaction with borane, may have more difficulty approaching the reaction center, especially in the polar solvent (THF) which forms the borane/THF complex.

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